

KINETICS, MECHANISM AND PRODUCT YIELDS IN THE ATMOSPHERIC OXIDATION OF DIMETHYLSULFIDE

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LONG-TERM GOALS

Dimethylsulfide (DMS, CH_3SCH_3) produced by phytoplankton emission is thought to be the major source of the sulfate and methanesulfonate aerosol found in the marine boundary layer. An understanding of the mechanism of formation of these aerosols is critical to understanding the factors which control visibility in the marine boundary layer. The primary objective of this research effort is the determination of the detailed mechanism of, and final products yields from, the OH initiated gas phase oxidation of dimethylsulfide (DMS).

OBJECTIVES

Our objectives include the determination of the elementary rates for adduct formation, decomposition and reaction. Direct confirmation of production, and quantitative product yields of potential reaction products such as sulfur dioxide (SO_2) and dimethyl sulfoxide (DMSO: $(\text{CH}_3)_2\text{SO}$). Determination of the homogeneous and heterogeneous removal rates of the stable primary products of DMS oxidation.

APPROACH

Our gas phase studies utilize the Pulsed Laser Photolysis-Pulsed Laser Induced Fluorescence (PLP-PLIF) technique. Laser photolysis of a suitable precursor, either H_2O_2 or HNO_3 , is used to generate OH. The rate of loss of OH, and the appearance of potential products such as SO_2 , SO and CH_3S are monitored by a second "probe" laser using laser induced fluorescence. Kinetic information is obtained by varying the delay between the photolysis and probe lasers, mapping out a temporal profile of the species of interest. Heterogeneous studies utilize an aerosol flow tube. We measure the rate of loss of SO_2 as a function of time and as a function of aerosol surface area. We use the TSI aerodynamic particle and scanning mobility particle sizers for aerosol measurements and laser induced fluorescence to monitor SO_2 .

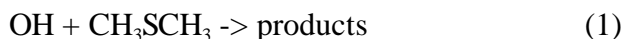
Report Documentation Page				Form Approved OMB No. 0704-0188	
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1. REPORT DATE 30 SEP 1997		2. REPORT TYPE		3. DATES COVERED 00-00-1997 to 00-00-1997	
4. TITLE AND SUBTITLE Kinetics, Mechanism and Product Yields in the Atmospheric Oxidation of Dimethylsulfide				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) University of Miami,Rosensteil School of Marine and Atmospheric Science,4600 Rickenbacker Causeway,Miami,FL,33149				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT Same as Report (SAR)	18. NUMBER OF PAGES 4	19a. NAME OF RESPONSIBLE PERSON
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified			

WORK COMPLETED

We have observed a large enhancement in the observed rate coefficient for the reaction of OH with DMS in the presence of nitric acid. These results cast some doubt on the currently accepted mechanism of the OH initiated oxidation of DMS. In an attempt to resolve these discrepancies our recent work has focussed on the forward addition rate for OHDMS adduct formation. We have two independent routes to these measurements. In the first we have attempted to measure the limiting rate enhancements in the OH+DMS rate coefficient at high nitric acid concentrations. We have made a number of these measurements however we need to complete a few more experiments on this system to ensure that NO₂ is not being generated by dark or heterogeneous processes. In the second approach we have measured the rate of vibrational deactivation of OH ($v=1,2$) by DMS, this work has been completed and was recently published (Silvente et al. 1997). Our ability to monitor these processes depends on our use of laser induced fluorescence at high sensitivity, monitoring OH via the A-X band at 282 nm. We have now discovered that an artifact is possible in such measurements of OH with sulfur containing species. If the metastable electronically excited state of diatomic sulfur, S₂(¹Δ) is formed with vibrational excitation i.e. in the $v=2$ level, an accidental spectroscopic overlap produces an interference signal. We have found that this artifact is present in the photolysis of gas mixtures of several sulfur containing molecules. We have made a detailed characterization of the spectroscopy of S₂(¹Δ) in the OH overlap region and examined potential routes to its formation. This work is essentially complete and is currently being written up.

RESULTS

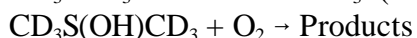
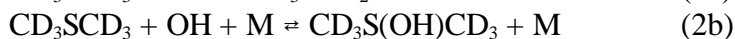
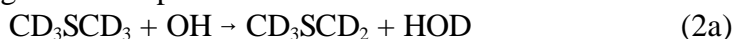
At the low NO_x levels that are characteristic of the remote marine boundary layer, reaction with OH is the initial step in DMS oxidation.



Hynes et al. (J. Phys. Chem. **90**, 4148, 1986) found that the effective rate of reaction 1 and its deuterated analogue, reaction 2,



is dependent on oxygen partial pressure and proposed that the reaction proceeds by a two channel mechanism, shown here for DMS-d₆, involving either hydrogen abstraction or OH addition to form a weakly bound adduct. The adduct can decompose to reform the reactants or react further with oxygen to form products.



Hynes et al. were unable to directly observe adduct formation. However, based on the assumed mechanism, they were able to estimate an elementary rate coefficient of $1.15 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for reaction 2b at 261K and 700 Torr. This estimate was based on the fact that the observed rate coefficient was similar in both 700 Torr of air and oxygen and had reached its limiting "O₂ enhancement". In earlier ONR supported work we reported the first direct observation of equilibration between OH and DMS-d₆ and obtained values for the adduct binding energy and the rate coefficient for its reaction with O₂ (Hynes et al 1995). This work was

performed at low pressure and reported a value of $6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 100 Torr at $\sim 250\text{K}$ in N_2 . For these results to be consistent, reaction 2b must have reached its high pressure limit at 700 Torr and the rate coefficient of $1.15 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ should be the high pressure limit, k_∞ . We have measured rate enhancements of up to $3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the reaction of DMS-d6 with OH at high nitric acid concentrations at 700 Torr. If the simple two channel mechanism is operative, this implies that the forward addition rate must be at least $3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, a value which is clearly incompatible with $k_\infty = 1.15 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Further support for a larger value of k_∞ comes from our measurements on the rate of vibrational deactivation of OH ($v=1,2$) by DMS. We obtain vibrational deactivation rates of OH ($v=2$); $(4.7 \pm 0.5) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$: OH($v=1$) $(2.5 \pm 0.3) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. This would suggest that the high pressure limiting rate of DMS/OH association is $\geq 5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

As noted above, if the metastable electronically excited state of diatomic sulfur, $\text{S}_2(^1\Delta)$ is formed with vibrational excitation i.e. in the $v=2$ level, an accidental spectroscopic overlap produces an interference signal when monitoring OH. We have found that this artifact can be produced in 266 nm photolysis of gas mixtures containing CS_2 , H_2S and COS. DMS does not appear to produce this artifact.

IMPACT

There have been no direct determinations of the rate coefficients for the elementary processes in DMS oxidation under conditions which are representative of the marine boundary layer. Such rates are required for a detailed model of the atmospheric oxidation mechanism. An accurate model of the oxidation process is critical in predicting new particle formation rates in areas in which DMS is the major precursor of condensation nuclei. Our results indicate a major inconsistency in the interpretation of laboratory results on the DMS oxidation process. If both the 1986 measurements of Hynes et al. and the more recent measurements reported here are all correct and the deactivation rates reflect the limiting adduct association rate, it implies that the simple two channel mechanism requires some modification. If the reaction of the OHDMS adduct with O_2 regenerates OH then rate coefficients which are measured by the PLP-PLIF technique underestimate the actual rate coefficients. Such an explanation could account for these discrepancies, but would require a large OH regeneration channel and would imply that the 1986 rate coefficients reported by Hynes et al. significantly underestimate the true rates. Direct measurements of the OHDMS adduct formation rate as a function of pressure up to at least one atmosphere and preferably up to the high pressure limit would do much to clarify this issue.

TRANSITIONS

The potential implications of this work for particle formation in the marine boundary layer will require a completion of the laboratory work and modeling studies.

RELATED PROJECTS

In our NSF sponsored work on HO_x cycling we have shown that the quantum yield for O^1D formation from ozone photolysis has a significant long wavelength component, part of which is

spin forbidden. This implies that current models underestimate OH concentrations, particularly at low temperatures and high zenith angles. Since DMS is a primary oxidant for both DMS and SO₂ these results will feedback into models of marine boundary layer chemistry and imply higher oxidation rates of both DMS and SO₂. In related ONR sponsored work we are attempting to develop novel laser based instrumentation to allow near real-time sodium measurements on individual, size-segregated marine aerosols. The development and deployment of such an instrument would improve our understanding of the size distribution of seasalt aerosols in marine air and provide data for relating the abundance of these aerosols to remotely observable parameters related to the physical state of the atmosphere and surface ocean. It would allow us to calculate the influence of sea salt-derived particles on the optical properties of the marine aerosol and characterize and predict the variability of this signal.

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